The Mechanism of Surfactant Effects on Drop Coalescence

B. Dai, A. Redondo and A. Graham
Los Alamos National Laboratory
G. Leal, University of California, Santa Barbara

Summary

Drop coalescence caused by collisions due to flow of a suspending fluid is dramatically hindered due to the presence of surfactants. The commonly accepted mechanism for this effect is that the fluid squeezed out of the contact region between adjacent drops generates a surfactant gradient. This in turn yields a Marangoni stress that is hypothesized to immobilize the interfaces and thus slow down the film drainage process that leads to coalescence. A scaling analysis based on an immobilized interface, however, is not consistent with recent experimental studies from Leal's laboratory at UCSB. Since the precise control of droplet size is of crucial importance in polymer blending and a number of other important technological processes, UCSB and LANL together initiated a multi-scale mathematical investigation of the detailed coalescence mechanisms. The critical physics, underlying this process, spans length scales from macroscopic to molecular, as the film rupture process is driven by van der Waals forces across the thin film.

For our initial study, we attempt to simulate the axisymmetric head-on collision and coalescence of a pair of equal size Newtonian (though polymeric) drops in a Newtonian (though polymeric) suspending fluid, in the presence of an insoluble (polymeric) surfactant. For simplicity in the analysis, the viscosity of the suspending fluid is assumed to be the same as the viscosity of the drops. Interfacial dynamics for Stokes flow can then be represented by a boundary integral of the unknown surfactant concentration function and its derivatives,

$$\mathbf{u}(\mathbf{x}_0) = \mathbf{u}^\infty(\mathbf{x}_0) - \frac{1}{8\pi Ca}$$
$$\int \mathbf{G}(\mathbf{x},\mathbf{x}_0) \cdot \left\{ \nabla_s \gamma(\Gamma) + \left[\Pi - \gamma(\Gamma)(\nabla \cdot \mathbf{n}) \right] \mathbf{n} \right\} ds(\mathbf{x}) \quad (1)$$

here $\mathbf{G}(\mathbf{x},\mathbf{x}_0)$ is the free space Green's function while the whole term in the curly bracket is the stress difference along the interface. The stress difference is induced by the capillary pressure $\gamma(\Gamma)(\nabla \cdot \mathbf{n})\mathbf{n}$, the Marangoni stress $\nabla_s \gamma(\Gamma)$, and the disjoining pressure $\Pi \mathbf{n}$ accounting for the van der Waals interactions at small scales. $Ca \equiv \mu GR/\gamma$ is the capillary number, which measures the relative magnitude of viscous to capillary forces, and $\mathbf{u}$ is the external flow. The drop shapes and positions are updated based upon the kinematic condition using the velocity calculated from equation 1.

With the presence of surfactants, the interfacial dynamics is fully coupled with the surfactant transport, e.g., equation 2, that is solved via a Galerkin finite element method. The interfacial surfactant concentration is constructed from a set of Lagrangian quadratic basis functions defined on the moving mesh determined by the interfacial dynamics, e.g., equation 1.

$$\frac{\partial \Gamma}{\partial \tau} - \mathbf{U}_{\mathbf{ref}} \cdot \nabla_s \Gamma$$
$$+ \nabla_s \cdot (\Gamma \mathbf{u_s}) - \frac{1}{Pe_s} \nabla_s^2 \Gamma + \Gamma (\mathbf{u} \cdot \mathbf{n}) \nabla \cdot \mathbf{n} = 0 \qquad (2)$$

where $Pe_s \quad GR^2/D_s$ is the interfacial Péclet number, the ratio of convective to diffusive flux and $\mathbf{U}_{\mathbf{ref}}$ accounts for the moving reference frame. A time-marching scheme is employed to exchange data between equation 1 and 2 for a convergence of both equations. Figure 1 shows the collision between two equal-sized drops with a uniform initial surfactant distribution in an axisymmetric, biaxial extensional flow. A surfactant gradient is built up along the interface and the interfacial dynamics is completely different from that of the clean interface due to the Maragoni stress induced by the surfactant gradient.

Our benchmark results show that during coalescence, the interface in the thin gap actually exhibits a significant degree of mobility. This explains, at least to certain degree, the fact that the scaling behavior based on the assumption of a completely immobilized interface is not in agreement with recent experimental measurements. The unexpected new result is that the role of Maragoni effects on the coalescence process does not occur via immobilization of the interface within the thin gap region, but rather due to its effects on the hydrodynamics outside the thin film. In particular, Marangoni streses immobilize the drop interface outside the thin film and this increases the total external hydrodynamic-force that pushes the drops toward each other. This, in turn, increases the degree of flattening and dimpling of the thin film, and it is primarily this change that slows the film drainage process and thus increases the required drainage time prior to coalescence.

Figure 1, the collision between two equal-sized drops with a uniform initial surfactant distribution along the center line in an axisymmetric, biaxial extensional flow (red: higher surfactant concentration; blue: lower surfactant concentration).

For further information on this subject contact:

Dr. Alan Graham
Los Alamos National Laboratory
graham@lanl.gov
505-663-5620

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*800-555-5555, imagenius@usnl.gov